California Environmental Protection Agency

Air Resources Board

Special Analysis Section
Northern Laboratory Branch
Monitoring and Laboratory Division

MLD SOP SAS04

STANDARD OPERATING PROCEDURE FOR WATER DETERMINATION IN CONSUMER PRODUCTS USING GAS CHROMATOGRAPHY

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1 INTRODUCTION

This procedure is used for the measurement of water in consumer products and is based on U.S. EPA Method 24/24A, Part 60, Title 40, CFR, Appendix A and ASTM D3792-91. Product samples are diluted with solvent and analyzed by gas chromatography. Any mention of brand names or commercial products is included as example only, and any equivalent product can be used.

2 SUMMARY OF METHOD

The samples of consumer products are prepared as a 1:10 wt./volume dilution in 1-Methoxy-2-propanol (MPA). After thorough mixing, the solution may require filtering to remove insoluble material. Some samples, particularly gels will require using the homogenizer unit to obtain sufficient surface area to determine the water. If under special circumstances another solvent is required, then all standards and controls are to be made with the same solvent and analyzed with those samples.

The diluted sample is then analyzed on a gas chromatograph equipped with a thermal conductivity detector to determine the water concentration in the sample. The data are reported as weight fraction of water in the product.

3 INTERFERENCES/LIMITATIONS

Compounds with retention times similar to water can interfere with this procedure. These can include dissolved aerosol propellant components.

4 APPARATUS

4.1 Glass vials (10 mL) with Teflon-lined caps

4.2 Stainless steel column, 6’ X 1/8" o.d., packed with HayeSep C, 80/100 mesh, or any analytical column capable of separating water from all possible interferences and showing a sharp, clean peak that will allow the analyst to achieve a desired detection limit

4.3 Gas Chromatograph (GC) configured with a Thermal Conductivity Detector (TCD)

4.3a. GC Parameters are as follows:

Time: Oven Conditions:	
Initial Temperature:	80 ^{o}C
Initial	1.20 min

Rate:	20.0 °C/min
Final Temperature:	210 °C
Final Time:	6.20 min
Oven Equilibration:	0.3 min
Injector Temperature:	250 °C
TCD Detector Temperature:	250 °C
TCD Sensitivity:	Low
TCD Polarity:	+
Peak Width:	0.053 min
Data Rate:	5.00 Hz
Column Flow Rate:	30 cc/min
TCD Reference Flow Rate:	45 cc/min

4.4 Volumetric Flasks, 10 mL

4.5 Analytical balance capable of weighing to the nearest 0.001 gram

4.6 Rainin pipettors, 2.5 mL and 1.0 mL with pipette tips

4.7 Small disposable pasteur pipettes with bulbs

4.8 GC vials and caps

5 REAGENTS AND MATERIALS

5.1 1-Methoxy-2-propanol (MPA)

5.2 Water: ASTM Type I

5.3 Calibration standards: Five calibration standards are prepared by diluting 0.100, 0.200, 0.400, 0.600, and 1.00 gm ASTM type I water to 10 mL with MPA

5.4 Helium: Grade 5

6 PROCEDURE

6.1 The samples are prepared as 1:10 dilutions in MPA. Using a 1.0 mL pipette, weigh to the nearest 0.1 mg a well mixed 1.0 mL aliquot of the product into the 10 mL volumetric flask. Record the weight in the dilution weight logbook. Bring to volume with MPA, mix well, homogenizing if necessary, and transfer to a 10 mL screw-capped storage vial. A check sample and a trip sample are also prepared as 1:10 dilutions in MPA.

6.2 Calibration: A five-point linear regression calibration is made (See 5.3).

6.3 Transfer an aliquot of each standard into appropriately labeled GC vials and cap.

6.4 Transfer an aliquot of each sample into appropriately labeled GC vials and cap. Also, transfer aliquots of the check and trip samples into appropriately labeled GC vials and cap.

6.5 Aliquot MPA into an appropriately labeled GC vial and cap. This sample will be your MPA blank.

6.6 Place the vials in the autosampler in the following order: MPA blank, calibration standards, MPA blank, check sample, trip sample, and diluted samples. The check sample is run every tenth sample and at the end of the run.

6.7 In the HPChem software, edit the SEQUENCE parameters appropriately.

6.8 Run the sequence.

7 QUALITY CONTROL

7.1 An MPA solvent blank must be analyzed for each batch of samples. The water concentration in the solvent blank must be less than 0.1% wt./volume.

7.2 A check sample (25% wt./vol. water) is run after the calibration, after every ten samples and at the end of the run. The result must be recorded on the procedure Control Chart and must fall within $\pm$ 3s of the control limits.

7.3 A trip sample of known concentration (60% water $\pm$3%) is also analyzed.

7.4 The five-point calibration curve must have a correlation coefficient of greater than 0.98.

7.5 The LOD for the water analysis should be determined annually. The LOD for this method is 1.0 mg/mL.

8 CALCULATIONS

The weight fraction of water in the product is calculated as follows:

$$\text{Weight Fraction Water} = \{H_2O \text{ (mg/ml)} / \text{sample dilution weight (g)}\} \times 10^{-2}$$

9 REFERENCES

9.1 ASTM Method D3792-91, "Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" (EPA Method 24).

9.2 "Determination of Volatile Organic Compounds (VOC) in Water Based Aerosol Paints". Bay Area Air Quality Management District Method 36, August 31, 1990

APPENDIX A

GC WATER PROCEDURE: OPERATION OF THE 5890

1. GC/Water analysis is run on the HP 5890, using injector A (front) and detector A (the TCD).

2. Preparation of Calibration Standards:

   Weigh into 10 mL volumetric flasks ASTM Type 1 water (from the Nanopure system) as follows:

10 mg/mL	0.10 g
20 mg/mL	0.20 g
40 mg/mL	0.40 g
60 mg/mL	0.60 g
100 mg/mL	1.00 g

   Bring to volume with MPA and store the individual standards in screw-cap vials.

3. Check Sample:

   A check sample of 25 mg/mL water is analyzed after the calibration, after every ten samples, and at the end of the run. A stock solution of 25% acetone/water in MPA is kept in the refrigerator. The check is prepared as a 1:10 dilution of the stock. Pipette 1.0 mL of the stock solution into a 10 mL volumetric and bring to volume with MPA. Store the check sample in a 10 mL screw-capped vial. The water check stock solution is prepared by weighing 50g each of acetone and water into a 200 mL volumetric flask and bringing to volume with MPA. Note: the water and acetone were weighed out in the preparation of the stock, so the concentration is already g/mL.

4. Trip Sample:

   A trip sample of known concentration is carried out with the procedure. The trip sample stock standard is stored in 20 mL vials and kept in the refrigerator. One is taken with the sample set. The trip sample is prepared as a 1:10 dilution of the stock. Pipette 1.0 mL of the stock solution into a 10 mL volumetric flask and bring to volume with MPA. The trip sample stock solution is prepared by weighing 300 g of water, and 50 g each of NaCl, acetone, methanol, and ethanol into a 500 mL volumetric flask and bringing to volume with MPA.

5. Samples:

   Weigh a 1 mL aliquot of the sample into a 10 mL volumetric flask and bring to volume with MPA. Record the weight in the dilution weight logbook. If the sample is a gel, the homogenizer may be used to aid in the mixing of the sample dilution. All samples are prepared as 1:10 dilutions in MPA. The same dilutions are used for the Karl Fischer Acetone/Alcohol, DCM, Siloxane, and MEK analyses. Transfer the diluted sample into a 10 mL screw-capped storage vial.

6. Using disposable pipettes transfer the MPA blank, standards, check, trip, and samples into appropriately labeled GC vials and caps.

7. Check that there is sufficient He (the carrier gas) for the run. The tank should be changed when the pressure regulator indicates 500 psi or less.

8. The GC conditions and settings are as follows:

Column:	Hayesep C 80/100 mesh 6ft x 1/8th in. od stainless steel packed column
Oven Temperature:	80 ^{o}C
Init Time:	1.20 min
Rate:	20.0 ^{o}C/min
Final:	210 ^{o}C
Final Time:	6.20 min
Injector Temperature:	250 ^{o}C
Detector Temperature:	250 ^{o}C
Det A TCD ON [+]	
TCD A: LOW SENS	
EPP A:	28.3 psi at 80 ^{o}C

9. Verify that you have loaded the water method in the system. In the HP CHEM station, click on Method; then click on Load. The method used is **WATER**. Highlight WATER, then press LOAD.

10. Modify the sequence as necessary. The sequence used is called **water**. Click on

SEQUENCE, then highlight WATER, and LOAD. Then click on Sequence, Edit Sequence Parameters to create a subdirectory for the data.

--Enter in Subdirectory a data file path, Yr/Mon/Day
e.g., 961016A (the letter is used to designate another data file if there is already one of the same date.)

11. Edit the Sequence table, click on:

--Sequence
Sequence Table
Injector, FRONT

Under Sample Name, enter the MPA blank, the five standards, the blank again, the check, the trip, and the samples. An MPA blank followed by the check is run after every ten samples and again at the end of the run. The method is WATER and the vial number corresponds to the position on the autosampler tray. Place sample vials in the autosampler in the following order: MPA blank, calibration standards, check standard, trip sample, and diluted samples.

Each vial will have its own vial number, but the sequence number is just the line item number in the table. To run the blank and the check multiple times, just insert the vial number, it is not necessary to prepare a separate vial.

12. Check to be certain everything has been entered correctly. Press SAVE in the Water sequence. Print the Sample Log Table.

13. To start acquisition click on:

-----RUN CONTROL
Run Sequence

14. Record the sequence, blank, checks, trip sample, and any observations in the instrument lab notebook. The correlation coefficient for compounds present in the calibration must be greater than 0.98. If the calibration fails, the sequence is stopped and corrective action is implemented. Corrective action can include reanalyzing the calibration curve or making up a new dilution of the calibration curve and then reanalyzing.

15. After the sequence is complete, verify that the check sample recoveries are within control limits. If the check is not within the control limits, re-run the analysis for the affected samples. It may also be necessary to recalibrate and rerun the affected samples. Record the check value on the appropriate control chart. Also indicate if there is anything detected in the blank. Print out the calibration curve for the standards.

16. Review the chromatograms. Check the MPA peak to be certain it is approximately the same height throughout the analysis. If a sample was misinjected, the problem will most likely show up in the MPA peak. Calculate the value for each analyte found by dividing the amount from the report (mg/mL) by the sample dilution weight.

17. Verify that the trip sample recovery is correct (60% water). The recovery for the trip sample should be within the error of the method (± 3%).

18. Note any problems in the lab notebook.

19. Place the chromatograms and the calibration in a folder labeled with the sample numbers. Place the file in the designated file drawer.

SOP REVISION HISTORY

DATE	VERSION	NOTES
May 16, 1996	1.0	Addition of trip samples to QC.
March 10, 1998	1.1	Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.
January 4, 2003	1.2	Renumbered to new section number. Adjusted document font to Times New Roman 12. Modified calibration curve concentrations (changed 80ug/ml to 100ug/ml).
September 5, 2003	1.3	Corrected typographical errors. Corrected version enumeration.